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This report describes the progress that has been made over the last years toward the generation of ultrashort electron pulses, and their application to time-resolved electron diffraction. We have generated electron pulses of picosecond duration using an ultrafast laser system, tested a number of photocathode materials, built an apparatus to measure electron pulse durations in the femtosecond domain, and designed and built an electron diffractometer for time-resolved electron diffraction. We demonstrated that the diffractometer, which uses a novel one dimensional detection scheme, is well capable of determining atomic distances in molecules to better than on hundredth of an Ångstrom. A sophisticated noise suppression system maintains a signal to noise ratio sufficient for pump-probe experiments. Further developments include the design of a reflectron electron gun for femtosecond electron pulses, and a two dimensional electron diffraction detector. Finally, significant progress has been made in the interfacing of adaptive optics to a learning algorithm, and the generation of spectrally tunable ultrashort laser pulses at 200 nm.

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Final Progress Report

Peter M. Weber,

31 December 1995

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Abstract

This report describes the progress that has been made over the last years toward the generation of ultrashort electron pulses, and their application to time-resolved electron diffraction. We have generated electron pulses of picosecond duration using an ultrafast laser system, tested a number of photocathode materials, built an apparatus to measure electron pulse durations in the femtosecond domain, and designed and built an electron diffractometer for time-resolved electron diffraction. We demonstrated that the diffractometer, which uses a novel one dimensional detection scheme, is well capable of determining atomic distances in molecules to better than on hundredth of an Ångstrom. A sophisticated noise suppression system maintains a signal to noise ratio sufficient for pump-probe experiments. Further developments include the design of a reflectron electron gun for femtosecond electron pulses, and a two dimensional electron diffraction detector. Finally, significant progress has been made in the interfacing of adaptive optics to a learning algorithm, and the generation of spectrally tunable ultrashort laser pulses at 200 nm.

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1. Summary

The focus of our research is the generation, characterization and optimization of ultrashort pulsed electron beams on the one hand, and the application of such electron beams for the benefit of science and technology on the other hand. During the 3 year funding period an extensive scientific and technological foundation has been laid. Some of our findings have been detailed in 3 publications; 4 papers have been submitted for publication, and several others are currently being written. This report highlights the experimental equipment that has been assembled, and illustrates some of the scientific and technological results.

2. Outline and motivation of the research project

Electron beams are used in a great variety of scientific and technical instruments. Most of those electron beams are continuous, being generated using thermionic emitters. Our research project stems from the realization that it is possible to generate ultrashort electron pulses using an ultrashort laser pulse, by photoemission from a metallic photocathode. The ultrashort electron pulses may, just like ultrashort laser pulses, find many applications in science, and also in the engineering of novel high tech devices. It is our goal to optimize the generation of electron pulses, characterize their properties, and apply them to interesting problems that could not be solved with other means. Within this framework, the specific goals of our work are:

Generation of pulsed electron beams

It is our goal to make ultrashort electron pulses a tool that is routinely available to the entire community. We are testing photocathode materials for electron emission efficiency in order to maximize the electron current, and to select environmentally stable cathodes. Our current favorites are gold and copper cathodes, which, surprisingly, work well even though the laser radiation has a photon energy below the work functions of those metals.

Measurement of electron pulse durations:

The scope of this project is to explore methodologies to measure ultrashort electron pulses containing very few electrons. We have assembled an apparatus to observe the cross correlation between a laser pulse and an electron pulse. The experiment will be performed in the near future.

Measurement of short lived molecules and molecules in transient states:

We apply the ultrashort electron pulses available in our laboratory to investigate the structures of molecules in short lived and transient states. The molecules are seeded in a molecular beam, and electronically excited by a short laser pulse. New molecular structures may arise because the prepared excited state has a potential energy surface that differs from that of the ground state, because intramolecular dynamics during the chemical reaction changes the structure, or because fragments generated by the reaction have different structures than the reactants. In general, the only methods to observe molecular structures are diffraction and rotational spectroscopy. While spectroscopic measurements have been performed on many molecules, they are not applicable whenever the lifetime of the investigated structure makes spectral resolution impossible. Typically, the Heisenberg Uncertainty relation prohibits rotational resolution for lifetimes in the picosecond regime. Our diffraction experiment is not limited in this fashion, because there is no position - time uncertainty that would restrict the temporal resolution of structure measurements. The electron diffraction experiments are therefore expected to provide magnificent insight into the pathways of chemical reactions.

Inversion:

In a collaborative project with Prof. Herschel Rabitz, Princeton, we are preparing to apply the time-resolved electron diffraction experiments to derive intramolecular potentials. We shape the laser pulse that excites the molecule, and observe the time dependent response of the molecule using diffraction. A learning algorithm continually shapes the laser field until an optimal focusing of the molecular wavepacket to a certain structure is achieved. The shape of the laser field, which can be measured as described later, can then be inverted to yield the intramolecular potential energy surface. In principle, a similar experiment can be performed using spectral measurements; however, the structural data as obtained by electron diffraction is significantly easier to invert than the spectral data.

Related research projects:

There are two projects in our laboratory that are related to the ARO funded work, but supported by other sources. The first is a low energy electron diffraction experiment, funded by the Ford Foundation, and performed in collaboration with Prof. P. Estrup. We use the electron pulse technology to investigate the reconstruction dynamics of a surface that is heated by an ultrashort laser pulse. Later experiments will explore the reactivity of adsorbates. As is true for most of the equipment in our laboratory, the vacuum chamber that we have built for the LEED experiment exhibits some unusual features, and we collaborate with Balzers, Inc., in the test of a novel pumping scheme.

The second project employs a time-resolved two photon ionization scheme to measure time dependent photoelectron spectra of molecules in transient states. Clearly, the spectral information obtained in this experiment is complementary to structural data derived from the time-resolved electron diffraction experiment. The availability of both spectral and structural data will shed more light on the reaction pathways than the sum of either technique alone could provide. The photoelectron spectroscopy experiments have recently provided valuable information about the molecular orbital composition of excited electronic states in terms of zero order Born-Oppenheimer states.

3. Summary of the most important results

3.1. The Laser System

All our experiments use electron pulses of picosecond duration that are generated with an ultrashort laser system and metallic photocathodes. The central component of the laser system is an Argon-Ion pumped Titanium Sapphire laser (Spectra-Physics 'Tsunami'). A fraction of the Titanium Sapphire output is split off to seed a Positive Light 'Spitfire' regenerative amplifier, while the remainder is upconverted to the second harmonic in a BBO crystal and used to generate the photocurrent in our electron guns. The regenerative amplifier is pumped by a Positive Light Merlin Nd:YLF laser and generates 150 fs pulses of 12 μJ energy at a repetition rate of 50 kHz. The amplified output is upconverted to the fourth harmonic using sequentially an LBO crystal and a BBO crystal, and is used as the pump beam in the time-resolved gas phase electron diffraction experiments.

Several aspects of our laser system are noteworthy. First, it is very important for the laser beam that generates the electron beam to be extremely stable, so that laser power fluctuations do not add noise to the electron diffraction pattern. We addressed this problem by improving a commercial LCD light stabilization device. In collaboration with Cambridge Research, Inc., we tested a new feedback mechanism for their LCD stabilizer. We found the scheme to work very well, and measured a dc laser noise of less than 0.1 %. Secondly, laser pump - electron probe experiments were found to put high demands on the laser system: in order for space-charge effects not to broaden the electron pulse duration one needs a high repetition rate electron beam. Similarly, the digital timing electronics used

to record diffraction patterns require a repetition rate in excess of 10 kHz. On the other hand, the laser pulses must be sufficiently energetic to dissociate a reasonable fraction of the molecules in the target (>5%). These conflicting requirements led to the specification of a 50 kHz repetition rate for the regenerative amplifier, which indeed could be delivered by Spectra-Physics/Positive Light. We acted as a beta-site for this product, which is now commercially marketed.

3.2. Cathode material tests:

We constructed a vacuum apparatus to test photocathode materials. The goal of these studies was to find cathodes that exhibit a large electron yield at a wavelength conveniently available with the Titanium Sapphire laser system (second harmonic: ~400 nm). Furthermore, the cathode should be durable and environmentally stable. We tested a number of photocathodes, including indium-tin-oxide (ITO), lithium, lithium with a protective gold coating, magnesium, magnesium with gold coating, gold, and copper. Even though the work function of the latter two materials is above the photon energy of the second harmonic radiation, we observed a good electron yield. As the dependence of electron current on the laser power shown in figure 1 demonstrates, the electron emission proceeds via a two photon process. The two photon mechanism implies that the electrons are born with a kinetic energy distribution width of about 1 eV. This broad distribution is expected to increase the electron pulse duration. The exact amount of temporal broadening depends on the relationship between the electron energy and the emission angle. There are experiments in preparation at Brookhaven National Laboratory (Dr. Rao's laboratory) to measure angle resolved electron energy spectra, for both copper and magnesium cathodes. In considering the merits (environmental stability) and disadvantages (2-photon emission) of copper cathodes one has to remember that alternative materials, such as cesium or even magnesium, could also feature multiphoton emission of electrons. For our current electron guns we chose to stay with the copper cathodes, and deal with the pulse spreading in a different way (see the chapter on the reflectron, 3.6).

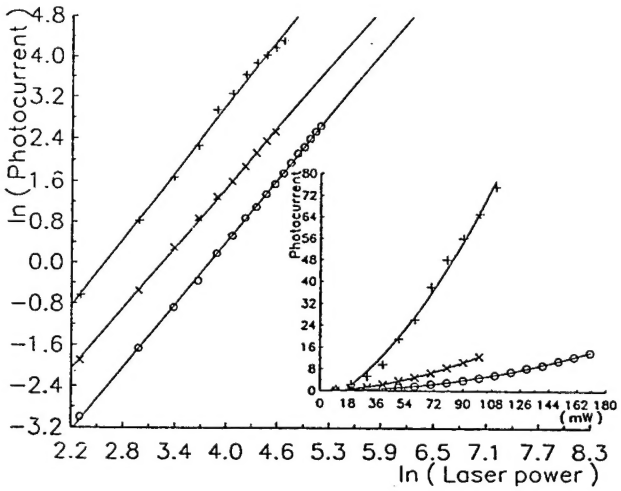

Figure 1: photocurrent generated by near UV photons at 386 nm (+), 408 nm(x), and 420 nm (o).

3.3. Tests of electron pulse durations:

An apparatus was assembled to measure electron pulse durations by electron-photon cross correlation. The operational principle is as follows. The electron pulse is generated in a vacuum apparatus using a copper photocathode, and accelerated to a window that has a thin gold coating. As the electron beam enters the gold surface it is expected to excite conduction band electrons to a transient, non equilibrium distribution. On the same surface a second electron beam is generated by another part of the femtosecond laser pulse. When the electron pulse entering the surface overlaps in time with the laser pulse that generates the second electron beam, then the photoelectron yield is expected to increase due to the non-thermal distribution of electrons. Varying the delay between laser and electron

pulses will allow us to record the desired cross correlation in the time averaged current of the second electron beam.

The experimental apparatus for this experiment is completely assembled. We tested the noise floor of the setup and found it to be sufficient to achieve the experimental goal. The experiment, which will use our amplified laser beam, is now on the agenda for the near future.

3.4. High Energy Electron Diffraction, 1-D detector

Using our proven cathode and electron gun design, we have built an electron diffractometer for time-resolved molecular structure experiments. The electron beam crosses the molecular sample that emerges from an effusive nozzle source, and a fraction of the electrons is scattered in the forward direction. In this electron diffractometer the analysis of the diffraction angle is achieved by an electrostatic deflector. The advantages of this unique detector are the low cost, good spatial suppression of undesired background radiation (electrons and x-rays), and further noise suppression by a narrow gate window in the timing electronics. The main disadvantage of the detector is that one can only record

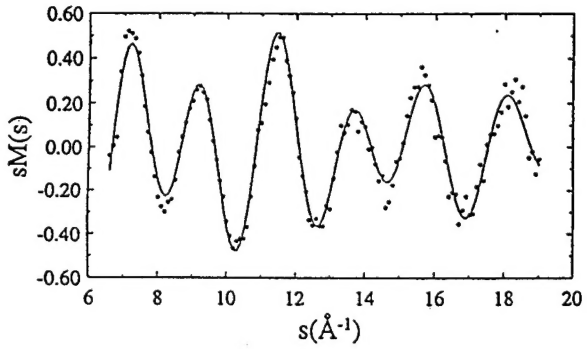

Figure 2: Diffraction pattern of carbon tetrachloride.

	$r_{C\text{-}Cl}$	$r_{Cl\text{-}Cl}$
Fit	1.771 Å	2.881 Å
Literature	1.766 Å	2.887 Å
Difference	0.005 Å	0.006 Å

Table 1: Interatomic distances obtained from the diffraction pattern of Figure 2.

one diffraction angle at a time, which leads to long data acquisition times and susceptibility to drifts in the photocathode current. After initial tests on a thin gold foil, we have now successfully applied the diffractometer to study the diffraction patterns of CCl_4, CH_2Br_2, CS_2, and several other molecules. Figure 2 shows the diffraction pattern of CCl_4, recorded at electron energies of 10 keV. The molecular parameters shown in table I demonstrate that very accurate interatomic distances can be obtained from such electron diffraction patterns.

We have described details of the operation of the diffractometer, the procedure for calibrating the deflector voltage to yield the diffraction angle, and the data reduction algorithm, in a recent publication [Geiser and Weber, 1995]. Tests of the noise levels of the diffraction patterns show that the signal to noise ratio is sufficient for subtracting diffraction patterns with the pump laser off, from those recorded with the pump laser on. The diffractometer is thus suitable for the planned time-resolved experiments.

3.5. High Energy Electron Diffraction, 2-D detector

For many structural measurements, and in particular for those experiments that seek to control molecular behavior, it is important that diffraction patterns can be recorded within seconds. For the reasons outlined above, our one dimensional detector is not suited for this task. We have therefore begun, with additional supported by a DURIP award through ARO, to construct an electron diffractometer with a two dimensional detector. In this detector the electrons impinge on a fluorescent fiber optic face plate (Schott), which emits photons at about 550 nm. A high quality lens system will image the diffraction pattern onto a CCD camera, which is interfaced to a Pentium computer. At the present time we are testing the efficiency of the face plate with the goal to determine the light intensity that is to be recorded by the CCD. These initial tests will help us to specify the noise level of the CCD, which then determines if a room temperature device suffices or if a cooled detector is necessary.

It is interesting to note that our research on the two dimensional detection of electron beams leads us away from microchannel and phosphor based devices, to ones with fiber optics and a CCD camera. It may be interesting to study the impact of our work on the design of night vision instruments, which use components and operational principles very similar to those employed in our experiments.

3.6. A Reflectron gun for generating femtosecond electron pulses

The two photon emission of electrons from the photocathodes described above leads to electron energy distributions of about 1 eV width. This large width increases the electron pulse duration at the target of interest. The electron energy distribution had been the most significant factor in increasing electron pulse durations even before we discovered this detrimental effect. A solution of the pulse broadening effects caused by the kinetic energy distribution was therefore considered very important. We have now completed design studies for an electron reflectron, a device that shortens the arrival time spread by compensating for the kinetic energy distribution in an electron reflector. Using electron trajectory calculations we have found the reflector voltages that minimize the electron pulse durations. Figure 3 shows the electron pulse duration obtained with the reflectron as a function of distance from the spatial and temporal focus. From these trajectory calculations we learned that electron pulse durations better than 200 fs are possible, even in the case of large kinetic energy distributions. An added benefit of the reflectron design is that it can partially compensate for space-charge effects that occur near the photocathode, while simultaneously rendering irrelevant those space-charge interactions that occur farther away from the photocathode.

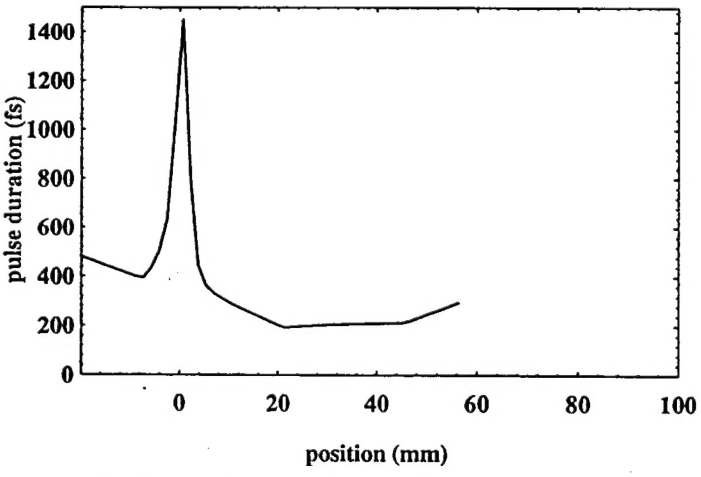

Figure 3: Pulse duration at the temporal focus of the reflectron. The spike reflects the position of the spatial focus, where the pulse duration is long.

3.7. Adaptive optics and genetic learning algorithms

As part of the program sponsored by ARO, through the presently discussed award as well as a DURIP award, we are developing a coherent control experiment with adaptive feedback. In essence, this experiment seeks to optimally control the structure of a molecule by exciting it with a tailored laser pulse. The structure obtained with a given excitation

pulse is fed into an adaptive learning algorithm, which optimizes the pulse shape to generate a molecular structure that most closely resembles the target structure. As a first step in this experiment we interfaced a spatial light modulator with an adaptive learning algorithm. Because the algorithm was developed in Hungary, by our collaborator Dr. A. Lorincz, one of the research assistants, Scott Carpenter, traveled to Hungary in the summer of 1995. We found that the learning algorithm can quickly learn to modulate the phase front of a laser beam to generate a specific change in the spatial beam properties. Some of the results have been submitted for publication, while others are currently being written up.

3.8. Spectrally shaped ultrashort laser pulses at 200 nm.

In order for coherent control experiments to be generally useful it is important to develop the experimental techniques to generate phase and amplitude modulated laser pulses at wavelengths where molecules absorb. To date, shaped laser pulses have been generated only in the wavelength range of the titanium sapphire fundamental, i.e., at about 800 nm. Unfortunately, there is almost no molecule with an absorption in this range. We have made significant progress in generating phase and amplitude shaped laser pulses at 200 nm by mixing a spectrally shaped IR pulse with a long duration UV pulse. The first results of this work have been submitted for publication.

4. List of publications, technical reports, and patent disclosures:

Publications with ARO support:

In preparation:

"Control of adaptive optics with a genetic Algorithm." With S. Carpenter, T. Szakacs, G. Szabo and A. Lorincz.

"Time-resolved surface electron diffraction." With H. Elsayed-Ali.

"Adaptive Optics Controlled by a Genetic Algorithm with Migration." With S. Carpenter, T. Szakacs, G. Szabo, and A. Lorincz.

Submitted for publication:

"Control of Adaptive Optics with a Genetic Algorithm." With S. Carpenter, T. Szakács, G. Szabo and A. Lorincz. Submitted to *CLEO 1996*.

"Generation of spectrally shaped, tunable, ultrashort laser pulses at 200 nm." With S. Carpenter, T. Lucza, G. Szabo and A. Lorincz. Submitted to *Ultrafast Phenomena 1996*.

"Extended operation of a wide-range, all-magnetic bearing turbomolecular pump without backing." With J.R. Thompson and R. Hellmer. Submitted to *J. Vac. Sci.Tech.*

"A novel detector for high repetition rate pump-probe gas phase electron diffraction." With J. Geiser and G. Seebohm. Submitted to *Rev. Sci. Instrum.*

Published:

"High Repetition Rate Time-Resolved Gas Phase Electron Diffraction." With J. D. Geiser. Proceedings, SPIE conference on Time Resolved Electron and X-ray Diffraction, July 1995, San Diego, Vol. 2521, p136.

"A Reflectron Design for Femtosecond Electron Guns." With S. D. Carpenter and T. Lucza. Proceedings, SPIE conference on Time Resolved Electron and X-ray Diffraction, July 1995, San Diego, Vol. 2521, p23.

"Pump-Probe Low Energy Electron Diffraction." With J. Thompson and P. J. Estrup. SPIE conference on Time Resolved Electron and X-ray Diffraction, July 1995, San Diego, Vol. 2521, p113.

Technical Reports:

Technical progress report to the ARO, 12/31/1993.
Technical progress report to the ARO, 12/31/1994.

Patent Disclosure:

"Intracavity Laser field shaping." Patent disclosure, filed with the Brown University Research Foundation.

5. Participating scientific personnel

Principal Investigator: Peter M. Weber

Graduate students:

J. Geiser; expected graduation: May 1997.

S. Carpenter; expected graduation: May 1997.

J. Thompson; expected graduation: May 1997.

B. Kim; (fall of 1994 only).

Scientific Collaborators:

Prof. Herschel Rabitz, Princeton University

Dr. Andras Lorincz, Institute of Isotopes, Hungary